**Pertanika 15(3),** 251-254 (1992)

# Micellization in a Mixed Alkali Soap System

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**Keywords: Micellization, sodium octanoate, sodium dodecyl sulphate, critical micelle concentration (cmc)**

**ABSTRAK**

*Keterlarutan natrium oktanoat dan natrium dodesil sulfat (SDS) di dalam larutan misel dikaji dengan mengukur ketegangan permukaan larutan surfaktan campuran sebagai fungsi pecahan mol surfaktan tersebut. Keputusan menunjukkan bahawa kepekatan kritikal misel untuk surfaktan campuran bernilai di antara nilai kepekatan kritikal misel kedua-dua surfaktan tulen tersebut. Keputusan juga menunjukkan perubahan nilai kepekatan kritikal misel berhampiran dengan nilai kritikal untuk rantai hidrokarbon yang lebih panjang. Dengan itu, dirumuskan bahawa rantai yang lebih panjang iaitu SDS lebih digemari dari segi geometri untuk pembentukan misel campuran. Keputusan juga menunjukkan bahawa natrium oktanoat dan natrium dodesil sulfat melarut secara campuran unggul.*

**ABSTRACT**

*The solubility of sodium octanoate and sodium dodecyl sulphate (SDS) in the micelle was investigated by measuring the surface tension of the aqueous solution of surfactant mixture as a function of mole fraction of surfactants. Results indicate that the critical micelle concentration (cmc) of the mixed surfactant falls between the cmc value of the two surfactants. The results also indicate that the rate of change of cmc value tends to be near the longer hydrocarbon chain molecule (SDS) with lower cmc value. Therefore it was concluded that the longer hydrophobic group of SDS is geometrically favourable for the micelle formation. In addition, the results indicate that SDS and sodium octanoate molecules mix ideally in the micelle solution.*

## INTRODUCTION

A previous paper (Hamdan *et al.* 1992) was concerned with the phase equilibrium and micelle formation of the mixture of sodium octanoate and sodium dodecyl sulphate (SDS), which are different in both hydrocarbon chain length and the structure of hydrophilic group at a ratio of 1:1 by weight. From the results, it was concluded that phase equilibria construction by the method employed was very tedious and time-consuming.

In this study the cmc (Shinoda 1963) value of various compositions of the mixed surfactant was used to try to further clarify the behaviour of the mixtures and predict the best composition to construct the phase equilibria.

The surface tension of aqueous solution of sodium octanoate and sodium dodecyl sulphate has been measured as a function of mole fraction at 30°C. The various cmc values of the mixed surfactant were then plotted against the mole fraction of the surfactant to determine ideality of the surfactant behaviour. The surface tension reported was only the apparent surface tension as the study concentrated on the composition rather than the absolute surface tension.

## MATERIALS AND METHODS

*Materials*

The surfactants sodium octanoate and sodium dodecyl sulphate (SDS) were obtained from Fluka and Sigma respectively. The SDS was recrystallized using absolute ethanol obtained from Sigma. Water used for the preparation of surfactant solution was doubly distilled.

*Determination of surface tension*

A Fisher (Model 215) surface tension analyser with sensitivity of 0.02 $mNm^{-1}$ employing du Nouy method was used for measuring the surface tension. Samples of 25 ml with various concentrations of surfactant were prepared and run at a speed of 0.00254 m $min^{-1}$. Pre-cleaned platinum-iridium ring with a circumference of 0.06 m attached to a wire of radius 178 μm was used. The temperature was controlled at 30 ± 0.01°C.

## RESULTS AND DISCUSSION

The experimental surface tension, γ versus logarithm of surfactant concentration curves observed at 30°C is shown in *Fig. 1-6.* The break point of the curve refers to the critical micelle concentration (cmc). These cmc values were then plotted against the mole fraction, α for the mixtures of sodium octanoate and sodium dodecyl sulphate as shown in *Fig. 7* and are compared to the theoretical curve obtained by using mixed micelle theory (Clint 1975) to check for ideality of the mixtures.

The mole fraction, α for component 1 is defined as described by the theory (Clint 1975). Here the components 1 and 2 are sodium octanoate and sodium dodecyl sulphate respectively. For the construction of phase equilibria, a graph of surface tension of micellar solution versus mole fraction of the mixture is predicted to have a minimum and the value is used as the composition of the mixture to obtain an ex-

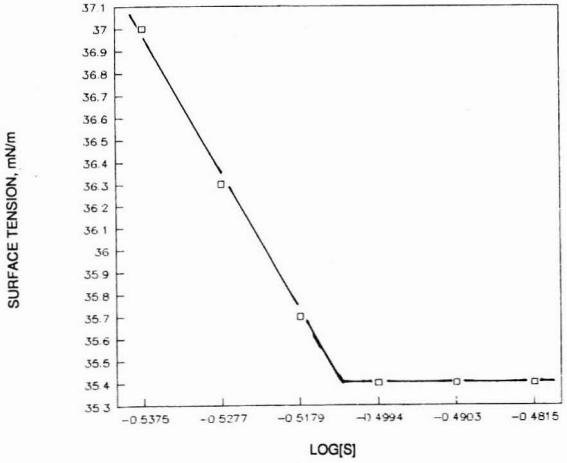


*Fig. 1: The surface tension, γ versus logarithm of concentration for sodium octanoate.*

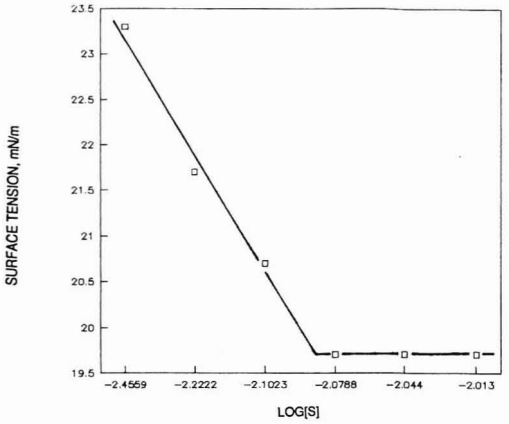


*Fig. 2: The surface tension, γ versus logarithm of concentration for sodium dodecyl sulphate*

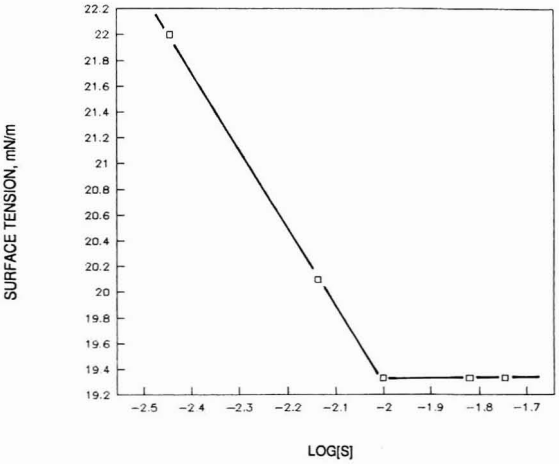


*Fig. 3: The surface tension, γ versus logarithm of concentration for mixture of sodium octanoate and sodium dodecyl sulphate (mole fraction of sodium octanoate = 0.16)*

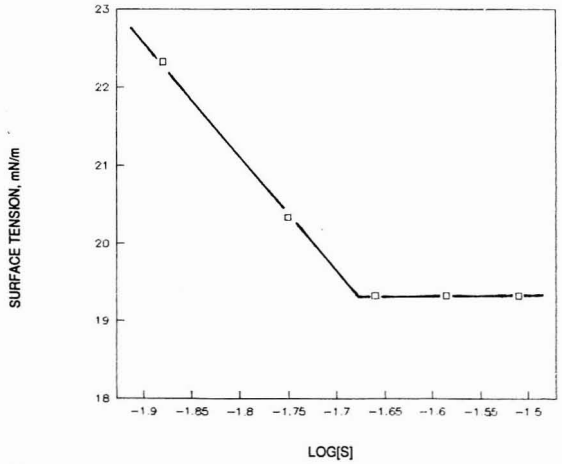


*Fig. 4: The surface tension, γ versus logarithm of concentration for mixture of sodium octanoate and sodium dodecyl sulphate (mole fraction of sodium octanoate = 0.64)*

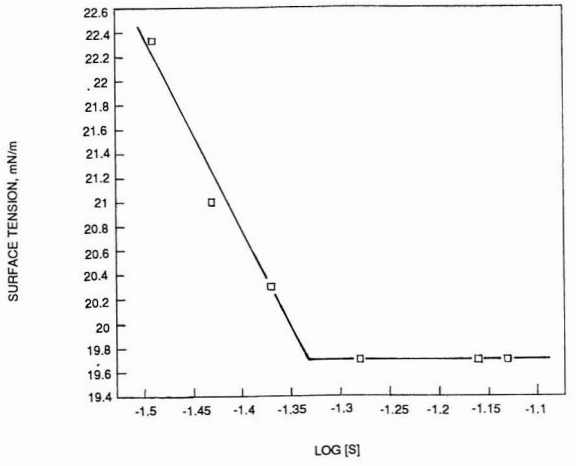


*Fig. 5: The surface tension, γ versus logarithm of concentration for mixture of sodium octanoate and sodium dodecyl sulphate (mole fraction of sodium octanoate = 0.87)*

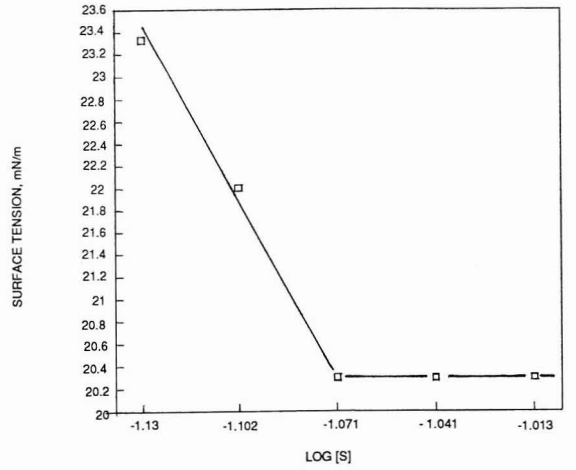


*Fig. 6: The surface tension, γ versus logarithm of concentration for mixture of sodium octanoate and sodium dodecyl sulphate (mole fraction of sodium octanoate = 0.94)*

tended lamellar liquid crystalline, D region.

*Fig. 1* and *2* show the experimental surface tension, γ versus logarithm of pure surfactant 1 and 2 concentrations respectively. The break point of the curve gives a cmc value of 0.008 and 0.31 mole/1 for the two surfactants. These values are referred to as $C_{M1}$ and $C_{M2}$ by the theory (Clint 1975) and are consistent with the value obtained by previous researchers (Ekwall *et al.* 1963; Evans *et al.* 1964; Mandell and Ekwall 1968).

*Fig. 3-6* show the experimental surface tension, γ versus logarithm of mixture concentration curves at mole fraction, α of 0.16, 0.64, 0.87

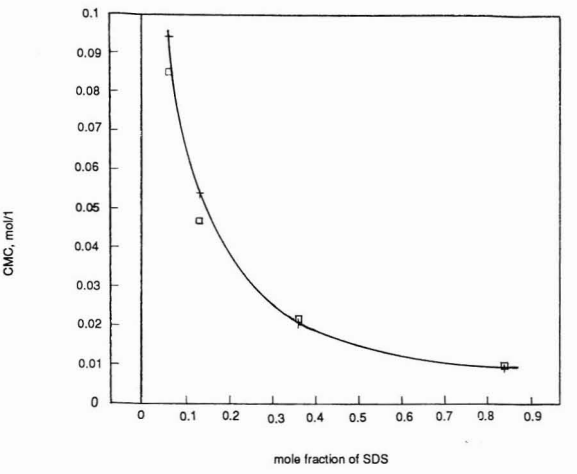


*Fig. 7: Variation of critical micelle concentration, cmc with mole fraction for mixtures of sodium octanoate and sodium dodecyl sulphate; □, experimental value and +, calculated value.*

and 0.94 respectively. A similar method was used to determine the cmc values of these mixtures. These values together with their corresponding surface tension, γ are tabulated as shown in Table 1. With that information available the behaviour of these mixtures becomes obvious. The cmc values are observed to be increasing with increasing mole fraction. The values also tend to be near the cmc value of sodium dodecyl sulphate. The surface tension, γ value of the mixed micellar solution is observed to change parabolically with an existence of minimum point as predicted earlier.

A graph of cmc versus mole fraction, α of mixtures was plotted as in *Fig. 7*. The theoretical value from the theory was calculated and plotted (*Fig. 7*). The experimental points are seen to be in good agreement with the theoretical ones. The curve (*Fig. 7*) also shows a negative deviation

TABLE 1
Experimental and calculated cmc values at various mole fraction, α of surfactant mixtures.

| mole fraction, α | $\gamma_{cmc}$,mNm$^{-1}$ | $CMC_{expt}$,mol/1 | $CMC_{theo}$,mol/1 |
|---|---|---|---|
| 0.16 | 19.33 | 0.010 | 0.0094 |
| 0.64 | 19.30 | 0.022 | 0.021 |
| 0.87 | 19.70 | 0.047 | 0.054 |
| 0.94 | 20.30 | 0.085 | 0.094 |

from ideality indicating a strong attraction towards the sodium dodecyl sulphate ions. This simple comparison of the mixtures of these surfactants is evidence for the assumption that the mixed alkali soap micelles behave as ideal mixtures.

The existence of a minimum in the surface tension of the micellar solution (Table 1) forms a striking interest and a graph of micellar surface tension versus mole fraction, $\alpha$ is plotted in *Fig. 8*. From the curve in *Fig. 8*, a value of 0.41 is selected as the composition of the mixture and is speculated to give a stable mixed alkali soap system with a large lamellar liquid crystalline region upon addition of an appropriate cosurfactant. This is however too early to predict as the stability of the system depends on factors such as:

1. The cmc value of the surfactant or mixture of surfactants
2. The slope of the adsorbed monolayer
3. The reduction in surface of interface tension after addition of surfactants.

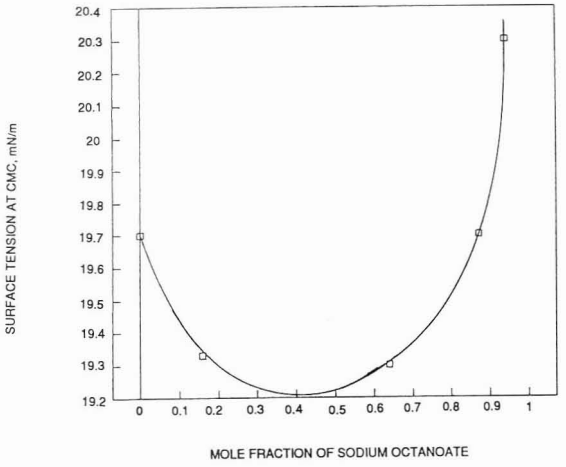


*Fig. 8: The micellar surface tension, $\gamma$ plotted against mole fraction for mixtures of sodium octanoate and sodium dodecyl sulphate.*

It appears the third factor is to be accounted for in this case because of the lowest reduction in surface tension. More information should be obtained by further examining the mixture of sodium octanoate and sodium dodecyl sulphate, for instance the thermodynamics of the micellization (Norihiro *et al.* 1992; Clint and Walker 1975).

It is however important to note that the mixtures behave ideally in accordance to the Mixed Micelle Theory and that the longer hydrophobic group of sodium dodecyl sulphate ion is geometrically favourable for the micelle formation.

## ACKNOWLEDGEMENTS

The authors wish to thank Universiti Pertanian Malaysia for supporting this work (Grant No. 50205). Special gratitude also goes to Dr. Hj Salleh Harun for allowing us to use the surface tension analyser and Mr. Rani Zaman for lending his technical support.

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*(Received 20 August 1992)*